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# Study of Fly Ash Characterization as a Cementitious Material

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**Abstract**

This research was conducted to compare class C and class F fly ash as cementitious materials. The fly ash was supplied by local power plants in Malaysia. The chemical composition analysis showed that class F fly ash has more Si and Al content compared to class C fly ash which affects the amount of the produced gel during the pozzolanic reactivity or/and geopolymerization. The chemical bonding analysis showed that class F fly ash has more bond structure (C–S–H, C–A–H, –Si–O–Al–, and –Si–O–Si–) than class C fly ash. Finally, the microstructure images indicated the similarity of the fly ash particles shape on both classes. Furthermore, the microstructure images showed a correlation between the chemical composition and the bond structure in terms of the high element content (Si and Al) forming the gel and the bond structure in the cementitious process during pozzolanic reaction or/and geopolymerization.


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*Keywords:* Powder; Paste; Chemical Composition; Chemical Bonding; Microstructure

## 1. Introduction

Fly ash (FA) is a fine particle comes from the combustion of pulverized coal in electric power generation plants [1]. During this process, most of the volatile substances and carbon in the coal are burned off. The mineral substance associated with coal crumble and the mineral impurities (such as clay, feldspar, quartz, and shale) are carried off in

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the form of ash by the exhaust gasses. From these processes, mainly two particle sizes are generated; the first is the coarser particles which contain heavier particles and first fall down to the furnace bottom. It is termed as the bottom ash. While the finer particles are flown together with the flue gasses and discharged to the air using a series of mechanical separators followed by highly efficient electrostatic precipitators or bag filters, so it is called as fly ash (FA) [2]. In 2013, it was recorded that Malaysia had produced more than 54 million metric tons of the FA and only 23 million metric tons (42.6% of the total FA) was used. The remaining amounts of 57.2% of the total produced FA were disposed in landfills [3]. The existence of such significant amounts forms a serious problem that has negative impacts on the society and the environment. Hence, the optimum utilization of the FA will contribute in solving this problem.

FA can be utilized in the concrete industry in two ways; the first is by using it as a partial replacement of cement based on its pozzolanic reactivity. The second is for total replacement of cement based on geopolymerization mechanism. In terms of the cementitious materials, the FA characteristics were mostly influenced by; the type and mineralogical composition of coal, the degree of coal pulverization, conditions during combustion, additives used to assist combustion or post-combustion processes, and the FA collected, handled and stored methods [4]. In general, FA consists of two categories refer to the total element of Si, Fe, and Al. Fly ash is classified as class C when the total content of these elements is more than 50%, and class F when it is more than 70%. Furthermore, FA is categorized into low calcium content (low Ca) and high calcium content (high Ca). For the low Ca type the Ca content should be in the range of 8-20% and for the high Ca the Ca content should be more than 20%. FA particles are spherical in shape and mostly glassy (amorphous) in nature with particles sizes less than 50 μm [4].

Referring to these characteristics, FA is known as a pozzolan material and in some cases as a self-cementitious material. In terms of pozzolan materials; FA is used as a partial cement replacement where the $Ca(OH)_2$ reacts with aluminate-silicate phase to produce calcium-silicate-aluminate hydrates [5,6]. This happens during the cement hydration associated with the presence of $SiO_2$ and $Al_2O_3$ in the amorphous form. On the other hand, FA is also used as a self-cementitious material in geopolymer cement where the FA is able to totally replace the cement. In this condition, the presence of aluminosilicate phases (from $SiO_2$ and $Al_2O_3$) produce the structural bond (-Si-O-Al-O-Si) based on the geopolymerization mechanism [5, 6]. Further studies are necessary in terms of FA characterization as a cementitious material considering the sustainability of this material and the ability to reduce its negative impact on society and environment, especially in Malaysia.

## 2. Material and experimental works

Two different types of FA powder were used in this research. The first was class C fly ash supplied by the electric generation plant in Manjung, Perak. The second was class F which came from the electric generating plant in Paka, Terengganu. It was classified according to the ASTM 618 standards requirement for the coal FA in terms of its chemical composition, particle size, and particle shape. The X-ray fluorescence (XRF) was used to find the chemical composition of the powder [7, 8], fourier transform infrared spectrometer (FTIR) was used for powder identification analysis [9, 10], and scanning electron microscope (SEM) was used to find the particle shape and the chemical reactivity of cementitious process [11, 12].

The paste was made according to the ASTM C305 standard procedures for mechanical mixing of cement paste and mortar [13]. Dry paddle and bowl were placed in the mixer and the mixing water (pozzolanic paste) or alkaline solution (geopolymer paste) was poured into the bowl. Binder powder was added into the bowl and kept for 30 seconds. Then, they were mixed at slow speed for 30 seconds after which it was stopped for 15 seconds. During the stop, the pastes were scraped from the side of the bowl and continued to mix on medium speed for 60 seconds. The fresh mix was poured into 50x50x50 mm steel cubic molds and each layer was tapped 16 times in two different directions to ascertain the removal of any air bubbles. The samples were taken from the mold after 24 hours and cured in water at temperature of 20 ± 2 °C for pozzolanic paste or cured at ambient temperature for geopolymer paste for 28 days.

## 3. Results and discussion

### *3.1. Chemical composition*

The chemical composition of both FA using the XRF powder analysis are shown in Table 1. The total element content of Si, Fe and Al in FA class C and class F was 61.71% and 91.35%, respectively. It can be seen that the Si and Al content in class F fly ash is more significant than class C fly ash and hence class F fly ash has more amorphous alumino-silicate than class C. this amorphous content reacts with the calcium hydroxide ($Ca(OH)_2$) released by the cement hydration processes to produce calcium-silicate-hydrates (C-S-H) gel and calcium-aluminate-hydrates (C-A-H) gel. Whereas, in terms of the geopolymerization process, it reacts with the alkaline solution to produce the aluminosilicate structural bonds (Si-O-Al-O-Si).

The Ca content in class C and class F fly ashes was about 27.1% and 1.32%, respectively. This means that class C fly ash is categorized as high Ca fly ash, while class F fly ash categorized as low Ca fly ash. The high Ca fly ash consists of the glassy rich calcium-alumino-silicate and various kinds of crystalline phases which are not found in the low Ca fly ash. It was noted that high Ca fly ash has higher reactivity compared to the low Ca fly ash and this can be seen from the short setting time in case of geopolymer past. This may be attributed to the reaction of some crystalline content with the alkaline solution which has more reactive nature of calcium bearing glass. While, the low Ca fly ash consists of alumino-silicate glasses has various amounts of quartz, mullite, hematite and magnetite. These crystalline phases are essentially passive, but it can react and form cementitious hydrates with the supporting of alkali or lime such as $Ca(OH)_2$.

Finally, both fly ashes have low alkali ($Na_2Oeq$) content. This means that these FA are not reactive as the alkalis in terms of higher pH of the pore solution in concrete so that it does not accelerate the dissolution of the glass in the FA.

Table 1: Chemical composition of class C and class F fly ash.

| Chemical composition of FA | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | $K_2O$ | $Na_2O_{eq}$ | $SO_3$ | MgO | LOI |
|---|---|---|---|---|---|---|---|---|---|
| Class C | 20.7 | 32.0 | 9.01 | 27.1 | 2.51 | 1.00 | 1.61 | 2.05 | 2.97 |
| Class F | 55.23 | 10.17 | 25.95 | 1.32 | 1.59 | 1.59 | 0.18 | 0.31 | 5.25 |

### *3.2. Fourier transform infrared spectrometer (FTIR) analysis*

It is known that there are six band ranges in the FTIR analysis. The band area detail of 4000-3500 $cm^{-1}$ indicates the loss of $Ca(OH)_2$, 3500-1600 $cm^{-1}$ indicates the stretching of the (-OH) bond and bending of the (H-O-H) vibrations, 1600-1000 $cm^{-1}$ indicates the gains of the Si-O-Si bond typical of quartz, 1000-800 $cm^{-1}$ indicates the loss of the $CaCO_3$ gel, 800-500 $cm^{-1}$ indicates the symmetric stretching of the Si-O-Si and Al-O-Si bonds, and the last band is less than 500 $cm^{-1}$ indicates the bending of the Si-O-Si and O-Si-O bonds [9, 10].

Table 2: Peak number of class C and class F FA

| Band range ($cm^{-1}$) | indication | Peak number | |
|---|---|---|---|
| | | Class C | Class F |
| 4000-3500 | Loss of $Ca(OH)_2$ | 0 | 0 |
| 3500-1600 | Stretching (-OH), bending (H-O-H) | 1 | 1 |
| 1600-1000 | Gains Si-O-Si bands typical of quartz | 1 | 1 |
| 1000-800 | Loss of gel $CaCO_3$ | 0 | 0 |
| 800-500 | Symmetric stretching of Si-O-Si and Al-O-Si | 1 | 3 |
| < 500 | Bending vibrations of Si-O-Si and O-Si-O bonds | 1 | 1 |
| Total band points | | 4 | 6 |

The FTIR analysis of the FA is shown in Figure 1 and Table 2. The different peak number between class C and class F is about 4 and 6, respectively. Nevertheless, they have same band area number. The similarity of the band area 3500-1600 $cm^{-1}$ indicates the (-OH) bond stretching and the (H-O-H) vibrations bending of bound water molecules which they are entrapped in polymeric framework cavities and absorbed on the surface, the 1600-1000 $cm^{-1}$ band indicates the gains in the Si-O-Si bands typical of quartz, the 800-500 $cm^{-1}$ band indicates the symmetric stretching of the Si-O-Si and Al-O-Si bonds which describes the formation of an amorphous to semi-crystalline alumino-silicate materials, and the band below 500 $cm^{-1}$ indicates the bending vibrations of the Si-O-Si and O-Si-O bonds (<500 $cm^{-1}$). It is noted for band range area of 800-500 $cm^{-1}$ which the peak number of class F is more than class C. It means that the formation of calcium-silicate-hydrates (C-S-H), calcium-aluminate-hydrates (C-A-H) and the structural bond (-Si-O-Al and -Si-O-Si-) of class F are more created than class C. These results conform the chemical composition of FA using the XRF analysis.

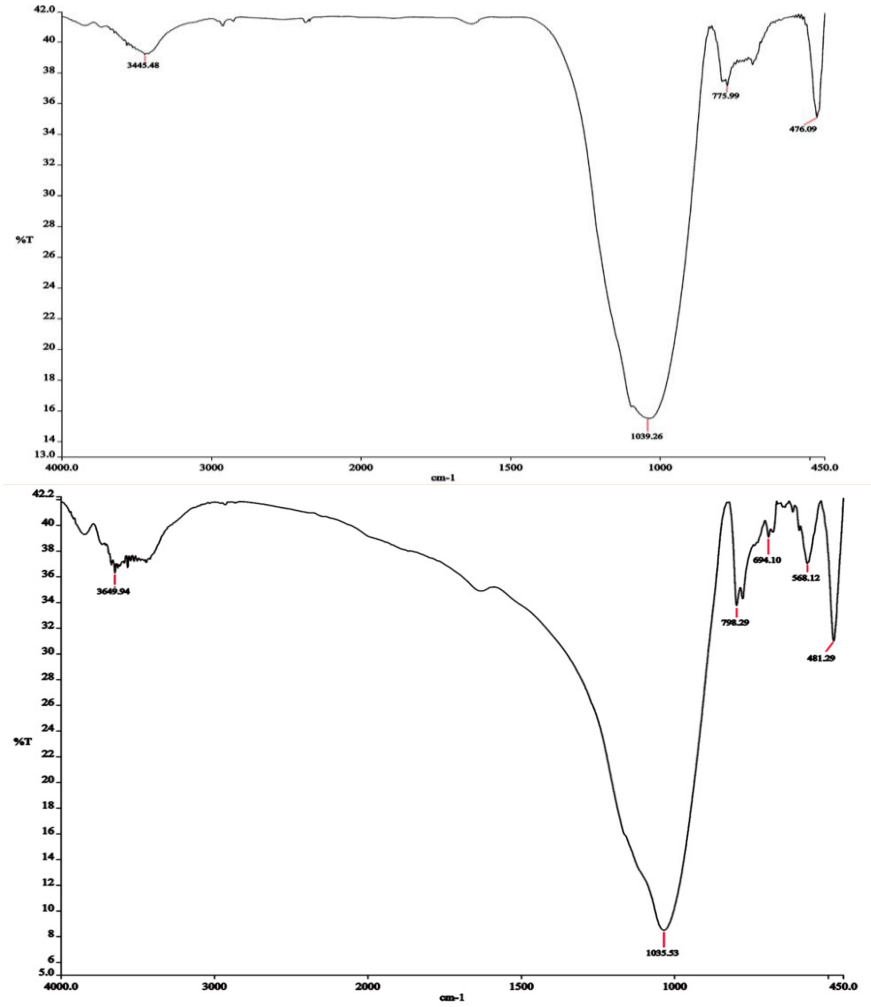



Fig.1. Powder FTIR analysis: (a) class C and (b) class F

### 3.3. Scanning electron microscope (SEM)

#### 3.3.1. Powder

In order to study the particle shape of FA, investigation via SEM/EDS was conducted as shown in Figure 2. It is obvious that there is no difference in morphology and elements between class C and class F fly ashes. The particle shape of FA is almost amorphous sphere and sleek which have over 50% chemical proportions of aluminum (Al), silica (Si) and oxygen (O) which they are in strong signal intensities. So that it is called as amorphous alumina-silicate sphere. While, the relatively weak signal intensities are in magnesium, potassium, calcium, titanium, and iron. This indicates the lower concentrations of the particles in these elements. However, this signal cannot conclude the percentage of chemical content as mentioned in XRF analysis, yet only indicates the signal intensities of the elements.

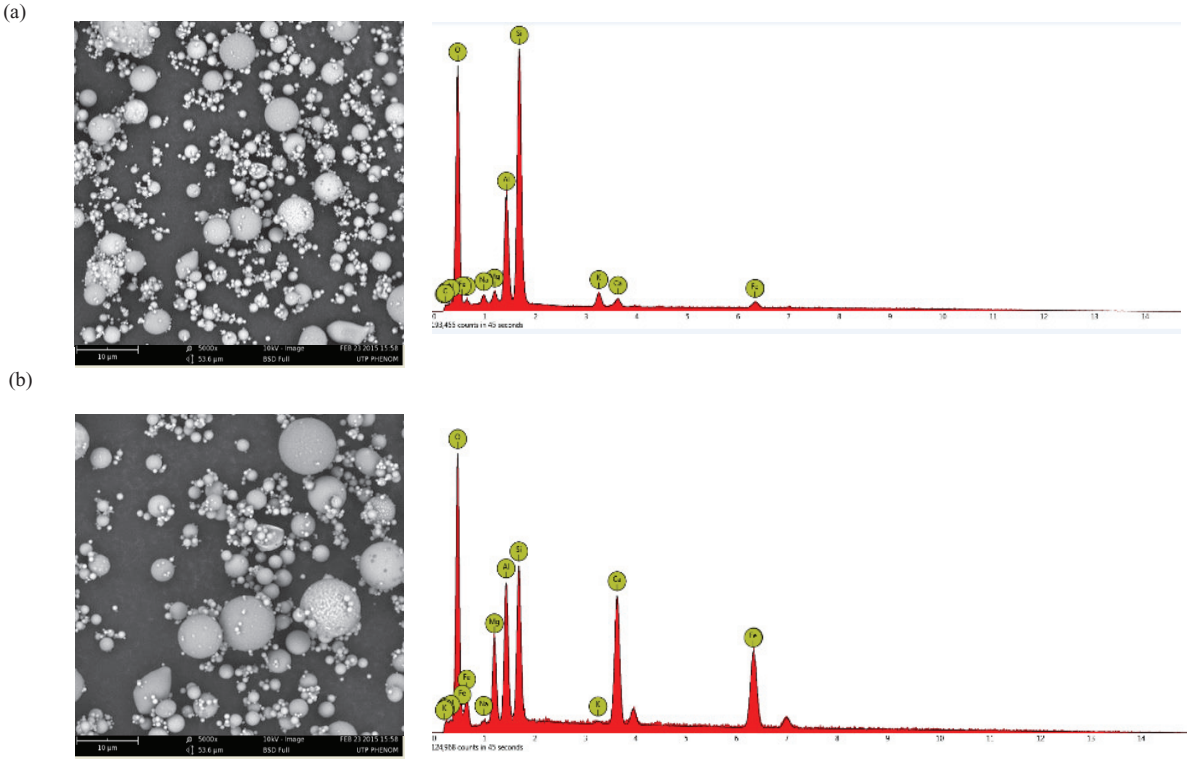


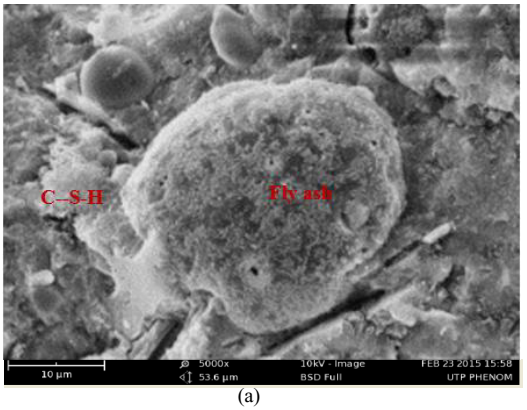

Fig.2. Powder FTIR analysis: (a) class C and (b) class F

#### 3.3.2. Paste

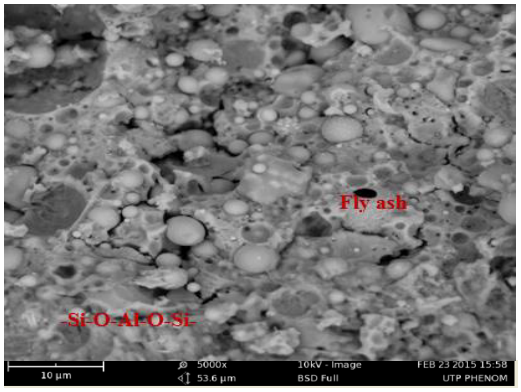
Figure 3 shows the image of the FA paste in pozzolanic reaction and geopolymerization. Figure 3a shows that the FA particles have three phases; the first phase consist of the particles with a dissolved surface indicating the precipitation in the pozzolanic reaction. In this condition, the FA are activated by $Ca(OH)_2$ which can substitute the FA particles with hydrates. The second phase is the hydration products where the pozzolan effect of the FA speeded up the reaction and increased the consumption of the C-S-H content. This is a result of the reactions between FA, $Ca(OH)_2$ and other hydration products. The third phase is the unreacted FA particles which can be seen as smooth spherical surfaces. These spheres serve as passive material that improves the packing effect and provides with

additional precipitation nucleus for hydration compounds that connect the cement particles and the FA, whereas the rest of the unreacted particles work as a filler in the paste.

Figure 3b shows the FA geopolymer paste microstructure. It is obvious the difference in the chemical reactivity between pozzolanic and geopolymer pastes. FA with the hollow spheres particle reacts with the alkaline solution forming a gel with a chemical bond (-Si-O-Al- and -Si-O-Si-). The reactive FA in geopolymerization is caused by the presence of Al and Si content. In addition, the unreacted or partially reacted FA particles create porosity in the matrix dispersed in small sized pores so cavities are found from the spaces left after the dissolve of the FA particles.




(a)




(b)

Fig.3. SEM analysis of FA paste: (a) Pozzolanic and (b) Geopolymerization

## 4. Conclusions

From the above descriptions it can be concluded that the chemical content of Si and Al of class F fly ash was more than class C fly ash and this also supported by the FTIR spectra analysis results. The chemical content will affect the forming of the (C-S-H) and (C-A-H) gel in pozzolanic reactivity and chemical bond (-Si-O-Al- and -Si-O-Si-) gel in geopolymer reactivity. Whereas, the unreacted FA particles served as filler in the cementitious process.

## References

[1] EIA, Annual Energy Review 2011, DOE/EIA-0384 (2011), Energy Information Administration, Washington, DC. Available from: http://eia.gov/aer, September 2012.

[2] ACAA, American Coal Ash Association 2013, Applications, Science, and Sustainability of Coal Ash 2013. Availability from: http://www.acaa-usa.org, 2013.

[3] EIA, International energy data and analysis of Malaysia, Energy Information Administration, Washington, DC Available from: www.eia.gov/beta/international/analysis_includes/countries_long/Malaysia, 2014.

[4] ASTM, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. 2012. C618.

[5] A. Favier, G. Habert, J.B. d'Espinose de Lacaillerie, N. Roussel, Mechanical properties and compositional heterogeneities of fresh geopolymer pastes, Cement and Concrete Research. 48 (2013) 9-16.

[6] J.E. Oh, Y. Jun, Y. Jeong, Characterization of geopolymers from compositionally and physically different Class F fly ashes, Cement and Concrete Composites. 50 (2014) 16-26.

[7] H. Kizhakkumodom Venkatanarayanan, P.R. Rangaraju, Decoupling the effects of chemical composition and fineness of fly ash in mitigating alkali-silica reaction, Cement and Concrete Composites. 43 (2013) 54-68.

[8] C. Monticelli, M.E. Natali, A. Balbo. C. Chiavari, F. Zanotto, S. Manzi, M.C. Binozzi, Corrosion behavior of steel in alkali-activated fly ash mortars in the light of their microstructural, mechanical and chemical characterization, Cement and Concrete Research. 80 (2016) 60-68.

[9] S. Puligilla, P. Mondal, Co-existence of aluminosilicate and calcium silicate gel characterized through selective dissolution and FTIR spectral subtraction, Cement and Concrete Research. 70 (2015) 39-49.

[10] I. García Lodeiro, D.E Macphee, A. Palomo, A. Fermandez Jimenez, Effect of alkalis on fresh C–S–H gels. FTIR analysis, Cement and Concrete Research. 39 (2009) 147-153.

[11] P. Chindaprasirt, U. Rattanasak, C. Jaturapitakkul, Utilization of fly ash blends from pulverized coal and fluidized bed combustions in geopolymeric materials, Cement and Concrete Composites. 33 (2011) 55-60.
[12] A.F. Abdalqader, F. Jin, A. Al-Tabbaa, Characterization of reactive magnesia and sodium carbonate-activated fly ash/slag paste blends, Construction and Building Materials. 93 (2015) 506-513.
[13] ASTM, Standard practice for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency. 2014. C305.